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DEVELOPMENT OF

FLY-ASH BASED GEOPOLYMER FOR CORROSION RESISTANT COATING

By

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Dissertation submitted in partial fulfillment of the requirements for the Bachelor of Engineering (Hons) Chemical Engineering Programme

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CERTIFICATION OF APPROVAL

Development of Fly Ash Based Geopolymer for Corrosion Resistant Coating

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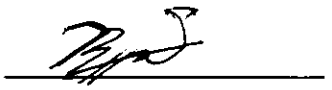
SEPTEMBER 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



BAHARUDIN BIN MAT HUSSAIN

ABSTRACT

Production of fly ash is 6 x 10^8 ton annually and is projected to increase. Only 20% is utilized in construction industry and the rest 80% goes to landfills. It had been reported that geopolymer has high resistance to corrosion attack. This project aims to investigate the feasibility of fly ash based geopolymer as corrosion resistant coating. The properties studied are compressive strength, setting time, chemical leaching, resistance to chemical attack, adhesive strength, water absorption, density change and microstructure evolution. Steel plates coated with the geopolymer had been tested in simulated corrosive environment. The geopolymer has high compressive strength, little chemical leaching, low water absorption, short setting time and increasing density pattern. Based on the results, it is believed that fly ash based geopolymer is feasible to be used as base material for corrosion resistant coating. Thusly, this project is a step towards increasing knowledge of industrial waste utilization by adding value to fly ash to convert it to geopolymer. Its success may benefit to reserve finances and at the same time to accentuate our affirmation in environmental guardianship.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Inorganic polymers, more commonly known as 'geopolymer', are alumina-silicate materials which demonstrate outstanding physical and chemical properties and exhibit a diverse series of potential applications. As it is costly using materials rich in silicon (Si) and Aluminium (Al), geopolymer work has mainly concentrated on the use of by-product or waste materials such as industrial wastes including coal fly ash, steel slag, palm oil fuel ash etc. and natural pozzolons in the geopolymer system. Further studies on these raw materials however are still required due to lack of more detailed scientific understandings and other concerns such as variations in mechanical properties, material characterizations, system parameters etc. (Divya et al., 2007).

Early researches have shown that geopolymers are cheap to produce and cost-effective solution to many problems. Due to the environmental concerns, there is growing demands for replacement of ordinary Portland cement (OPC) by using geopolymers given their numerous advantages including lower carbon dioxide emissions, thermal resistance and combined with enhanced mechanical properties both under normal and extreme exposure conditions (Esther et al., 2011). It has been reported that the wide use of geopolymer is expected to reduce the carbon dioxide (CO2) emission from the cement industries by almost 80% in comparison with OPC (Kostas et al., 2007). All these contributed to the huge development of research in geopolymerization for different purpose of applications.

Among those potential applications, geopolymer is believed to be utilized as novel coating materials due to its high performance in displaying the strength, fire resistivity, adhesiveness and durability which is comparable or better than that of existing coating materials (Jadambaa et al., 2010). Though this has been an important driving factor for global research, more intensive research efforts are required to position this novel technology within the industrial community.

1.2 Problem Statement

Using fly ash which is a waste of power generation industry greatly increase the significance of this project. Annual global production of fly ash is 6 x 10^8 ton out of which only 20 to 25% is utilized in the construction industry (Source: Concrete International May 1999 - M. Malhotra "Making Concrete Greener with Fly Ash"). Largely it is used as a partial replacement of cement for producing concrete. The remaining 75 to 80% is disposed n landfills (Source: Canadian Centre for Mineral and Energy Technology-CANMET). Besides being potentially hazardous to health, the disposal in landfills also mean more requirements for new land opening. Recently Jha et al. reviewed the potential of fly ash for the extraction of valuable metals, ceramic applications, synthesis of zeolite and manufacture of fire resistant materials. Research into geopolymers has identified their excellent mechanical properties, ability to encapsulate hazardous waste and high resistance to chemical attack. This mean geopolymer has the potential to be manufactured into corrosion resistant coatings. By using fly ash as the base for geopolymer to produce corrosion resistance coating, the corrosion problem can be combated and industrial waste can be efficiently reused that further leads to excelling environmental guardianship. Corrosion is a process that occurs when a material deteriorates due to its interaction with the surrounding environment in which an electrochemical reaction consumes the material through oxidation. The result of corrosion is degradation of material properties and manifests itself as component failure at the worst or unsightly appearance at the best and it's important to realize that corrosion occurs in nearly all systems and all operating environments. Corrosion can significantly impact readiness of the systems if excessive maintenance is required to ensure continued safe operation. Combating corrosion can be cost extensive, time consuming and requires expertise. A study which has been done in 2006 by Advanced Materials, Manufacturing and Testing Information Analysis Centre has estimated the cost at over $20B per year. Although employing corrosion preventive compounds and coatings may cost more initially, there are many potential benefits that will result including improved reliability, reduced maintenance, improved performance and efficiency, improved safety, increased service life, and reduced life-cycle cost. This project ultimately aims to address two main problems which are the industrial waste management and corrosion control.

1.3 Objective and Scope of Study

To the best of our knowledge, there are no reports on the application of fly ash based geopolymer corrosion resistant coating on metal substrates yet. The motivation for this research is to examine the feasibility of using fly ash for the manufacture of geopolymer corrosion resistant coatings on metal substrates, thus contributing towards efficient waste management by adding values to the fly ash by converting it to geopolymer.

The objectives of this project are:

1. To develop fly-ash based geopolymer for corrosion resistance purpose.
2. To study the properties of the developed fly-ash based geopolymer coating.
3. To optimize the properties of the fly-ash based coating.

Since there is non-existent literature on the application of geopolymer coating on metal substrates, this work is an approach in providing better understanding and better control on the synthesis of a novel coating material. In this project, the scope of study is to synthesize the geopolymer and will be followed by study of the effectiveness and suitability of fly ash based geopolymer for corrosion resistance coating. The scope of work involves laboratory experiments to study properties involved such as setting time, water absorption, porosity, chemical leaching, compressive strength and adhesive strength. The student focuses his study with executing the experiments according to procedures in the Chapter 3.This will be followed by analysis of results obtained which are presented in Chapter 4. The conclusion and recommendations are found in Chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1 Preface

The literature review can be divided into two subsections which include:

- The study on fly ash based geopolymer.
- The study on corrosion and basic approach to control it.

2.2 Introduction

Geopolymer is generically used as a term to describe the amorphous to crystalline reaction products from the synthesis of alkali alumina-silicates from reaction with alkali hydroxide or alkali silicate solution (Davidovits, 1991). The term geopolymer is probably more appropriately referred to as 'inorganic polymer' (Van Wazer, 1970). These materials can provide comparable performance to traditional cementitious binders in a range of applications, but with the added advantage of significantly reduced greenhouse emissions.

In concept of geopolymer, Davidovits (1988) has proposed that some of the major pyramids, rather than being blocks of solid limestone hauled into position, they are composed of geopolymers which is then cast in their final positions in the structure. In fact, it is reported that the Romans extracted volcanic ashes from volcanic craters for use in applications such as buildings, ports, roadways as well as irrigation systems. These historical buildings have their own aesthetic values but yet have also withstood the test of time (Barker L, 2000).

The geopolymer chemistry concept was invented in 1979 with the creation of a nonprofit scientific organization, the Institut de Recherchesur les Geopolymeres (Geopolymer Institute).According to Prof. Dr. Joseph Davidovits from his presentation in Geopolymer Conference 2002, geopolymers has several applications as listed in the next page since 1972.

1. Fire resistant wood panels
2. Insulated panels and walls,
3. Decorative stone artifacts,
4. Foamed (expanded) geopolymer panels for thermal insulation,
5. Low-tech building materials,
6. Energy low ceramic tiles,
7. Refractory items,
8. Thermal shock refractory,
9. Aluminum foundry application,
10. Geopolymer cement and concrete,
11. Fire resistant and fire proof composite for infrastructures repair and strengthening,
12. Fireproof high-tech applications, aircraft interior, automobile,
13. High-tech resin systems.

Even though geopolymers have been used in various applications, their widespread use is still restricted due to lack of detailed scientific knowledge and understanding as well as long term durability studies (Perera et al., 2004). Research in this field has historically been applications-focused and the mechanisms and processes underlying geopolymer formation have only relatively recently become the subject of detailed attention. The variation in mechanical and thermal properties is also a source of concern regarding the commercial and industrial maturity of geopolymeric materials.

It is shown that the raw materials and processing conditions are critical in determining the setting behavior, workability and chemical and physical properties of geopolymeric products. Depending on the raw material selection and processing conditions, geopolymers can exhibit a wide variety of properties and characteristics, including high compressive strength, low shrinkage, fast or slow setting, acid resistance, fire resistance and low thermal conductivity. Despite this wide variety of commonly boasted attributes, these properties are not necessarily inherent to all geopolymeric formulations.

Inorganic polymers should not be considered a universal choice for all material selection problems, but rather a solution that may be tailored by correct mix and processing design to optimize properties and/or reduce cost for a given application.

The main barrier that geopolymerization has to overcome is mainly related with the secure position of OPC in construction industry. Another issue that comes to mind is the conservative considerations from the industry to adopt with new technologies and products which likely will replace the existing ones. However, progress is being made in this area and the understandings that have been developed till now indicate the facts that geopolymer technology does have potential for wide scaled utilization in various industries.

2.3 Geopolymerization

Geopolymerization is a geo-synthesis where the reaction is chemically integrated minerals that involve naturally occurring silica-aluminates (Hermann et al., 1999). Geopolymers are formed through mixing solid alumina-silicate raw materials with highly concentrated aqueous alkali hydroxide or alkali silicate solutions which result in synthetic alkali alumina-silicate material. Geopolymer synthesis desires three main sources, namely raw materials, inactive filler and geopolymer liquor (Ikeda, 1998). Raw materials could be natural (alumina-silicate) minerals or industrial waste. Inactive filler, such as kaolinite or metakaolinite is used for the supply of Al^{3+} ions. Geopolymer liquor is an alkali hydroxide solution required for the dissolution of raw materials while sodium or potassium silicate solution acts as binder, alkali-activator and dispersant (Phair et al., 2001).

Geopolymerization is based on chemistry of alkali activated inorganic binders, which were accidently discovered by Purdon (Van Jaarsveld JSG et al., 1998). He summarized his study in two steps which are liberation of silica, alumina and lime and formation of hydrated calcium silicates, aluminates as well as regeneration of caustic solution. Similarly, Glukhovsky (1959) proposed a general mechanism for the alkali activation of materials primarily comprising silica and reactive alumina. The Glukhovsky model divides the process into three main phases, which are destruction-coagulation, coagulation-condensation and condensation-crystallization.

The mechanism highlights the key processes occurring in the transformation of a solid alumina-silicate source into a synthetic alkali alumina-silicate.

During geopolymerization, once the alumina-silicate powder is mixed with the alkaline solution a paste forms and quickly transforms into hard geopolymer. Therefore, there is no sufficient time and space for the gel or paste to grow into a well crystallized structure. After shorter setting and hardening time, geopolymers with tightly packed polycrystalline structure are formed exhibiting better mechanical properties which have lower density and cage-like crystalline structure (Xu and Van Deventer, 2000).

The process of geopolymerization involves leaching, diffusion, condensation and hardening steps and usually set at lower temperatures. Factors affecting the synthesis of zeolites include temperature, pH and cations and it is believed that these three factors also affect geopolymerization (Xu, 2001).

The geopolymerization reaction creates a polymeric backbone of aluminium and silicon atoms. Simplistically, geopolymerization engages the dissolution of alumina-silicate from the source material followed by short arrayed polymerization to form a polymeric structure of Si-O-Al-O which represents the main building blocks of geopolymeric structure. Figure 2.1 shows the geopolymeric structure.

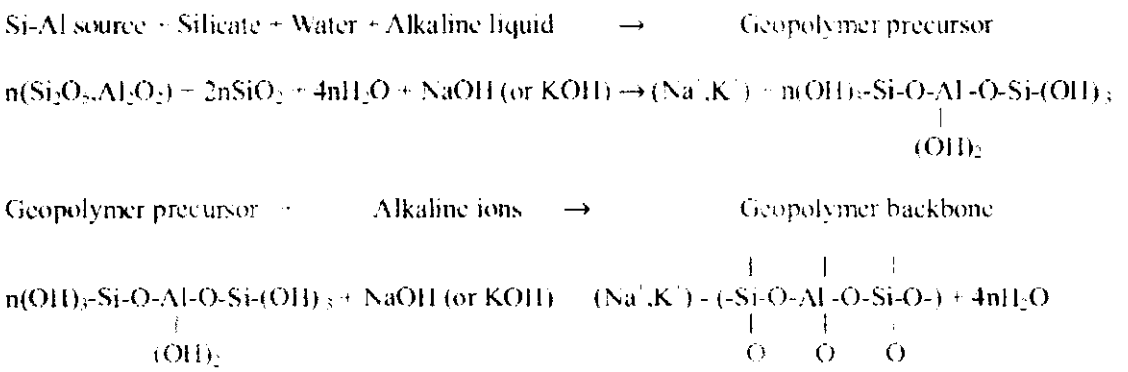

Figure 2.1: Geopolymeric Structure (Divya et al., 2007)

2.3.1 Raw Materials

Raw materials play an important role in the formation of geopolymer. Many studies have been conducted in order to develop various methods to improve durability of geopolymer. Various ranges of materials are presently being used in synthesizing the geopolymer. Any pozzolanic compound or source of silica and alumina that is readily dissolved in the alkaline solution acts as a source of geopolymer precursor species and thus lends itself to geopolymerization (Xu H and Van Deventer JSJ, 2000).

Davidovits (1984) primarily used kaolinite and metakaolin (calcined kaolinite) as source of alumina-silicate oxides in order to synthesizegeopolymers. Kaolinite provides structure forming species to the overall geopolymerization process. The addition of kaolinite is necessary since the rate of Al dissolution from the raw materials is insufficient to produce a gel of desired composition (Xu and Van Deventer, 2000). However, a large amount of added kaolinite may not take part in the synthesis reaction at all (Van Jaarsveld et al., 2002).

The use of metakaolin on the other hand improves mechanical strength and reduces the transport of water and salts in the final product (Kostas et al., 2007). In fact, geopolymers derived from metakaolin may require too much water due to porosity increase and thus becomes too soft for construction applications but it is important in the applications as adhesives, coatings and hydroceramics (Duxson et al., 2007).

The utilization of natural minerals, by-products and wastes was investigated extensively in later years. Xu and Deventer (2002) used fly ash, kaolinite and albite in various combinations for the synthesis of geopolymer. Astutininsh and Liu (2005) used milled Australian slag with CaO content. In 2007, Yusheng et al. tested the mechanical strength of blast furnace slag-metakaolin based geopolymer. Meanwhile, binder and coatings are the applications that are being studied in current years (Smith et al., 2010, Susan et al., 2011, Jadambaa et al., 2009, 2011, Zuhua et al., 2010).

Geopolymers are chains or networks of mineral molecules linked with co-valent bonds. They comprise following molecular units (or chemical groups): poly(siloxo), poly(sialate), poly(sialate-siloxo), poly(sialate-disiloxo), poly(phosphate), poly(phospho-siloxo), poly(phospho-sialate), and poly(organosiloxo).

Geopolymers are presently developed and applied in 9 main classes of materials:(book refers to Coatings Materials and Surface Coatings, Arthur A. Tracton, CRC Press,2007)

1. Waterglass-based geopolymer, poly(siloxonate), soluble silicate, Si:Al=1:0
2. Kaolinite / Hydrosodalite-based geopolymer, poly(sialate) Si:Al=1:1
3. Metakaolin MK-750-based geopolymer, poly(sialate-siloxo) Si:Al=2:1
4. Calcium-based geopolymer, (Ca, K, Na)-sialate, Si:Al=1, 2, 3
5. Rock-based geopolymer, poly(sialate-multisiloxo) 1<Si:Al<5
6. Silica-based geopolymer, sialate link and siloxo link in poly(siloxonate) Si:Al>5
7. Fly ash-based geopolymer
8. Phosphate-based geopolymer
9. Organic-mineral geopolymer

In this project, fly ash is used as the base for the geopolymer as the corrosion resistant coating material. Fly ash is a by-product of a coal burning furnace, usually from electric power generation equipment. It is classified as an industrial waste and poses potential health hazard because of the size of particles which is in the breathable limit. Consisting mostly of silica, alumina and iron, these fine, glass-like particles, when mixed with lime and water, form a cementitious material similar to Portland cement. The colour of fly ash can be tan to dark grey, depending upon the chemical and mineral constituents.

Fly ashes may be subdivided into two categories, according to their origin:

-Class F: Fly ash normally produced by burning anthracite or bituminous coal which meets the requirements applicable to this class. Class F consists of low calcium (CaO < 10%) and the total components of SiO_2, Al_2O_3 and Fe_2O_3 are more than 70%.

-Class C: Fly ash normally produced by burning lignite or sub-bituminous coal which meets the requirements applicable to this class. Class C fly ash may have lime contents (CaO) in excess of 10% and the total components of SiO_2, Al_2O_3 and Fe_2O_3 are more than 50%.

Fly ash can be activated by alkaline like NaOH so it can have cementitious property as that of cement. This cementitious property does not rely on calcium silicate hydration, but it is obtained from an inorganic polycondensation and so-called geopolymerisation. Evaluations done by Trenchless Technology Center in Louisiana Tech University shows that in term of corrosion resistance, Class F fly ash's absence of calcium oxide results in a superior performance compared to Class C fly ash. Class F fly ash from Tongshan Tongshun Industry from China is used to manufacture the geopolymer coatings.

Though many macroscopic characteristics of geopolymers prepared from different aluminosilicate sources may appear similar, their microstructure and physical, mechanical, chemical and thermal properties vary to a large extent depending predominantly on the raw material from which they are derived. Typical images illustrating the microstructures of geopolymers synthesized from metakaolin and Class F fly ash are presented in Figure 2.2. Large differences can be observed between the microstructures of these geopolymers.

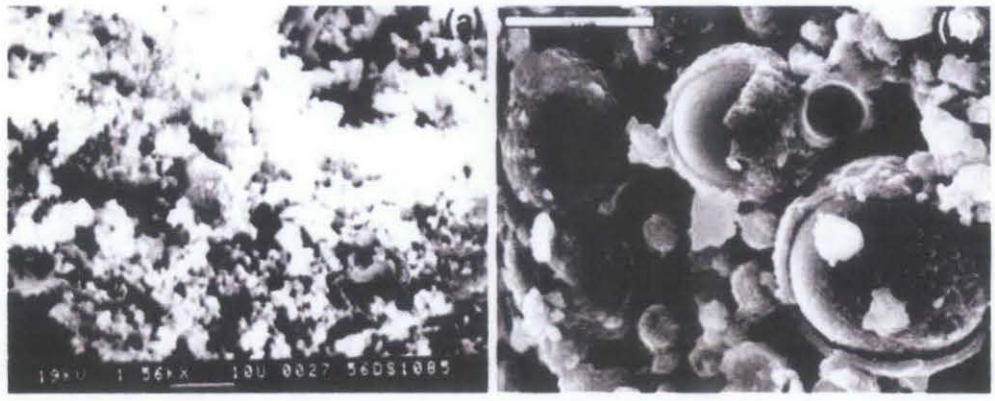

Figure 2.2: (a) Metakaolin activated with 8 M NaOH, (b) Fly ash activated with 8 M NaOH

Despite similarities in the molecular structure and nanostructure, the differences in the properties of geopolymers derived from different raw materials are clearly evident. Fly ash-based geopolymers are generally more durable and stronger. These traits often lead to the belief that the binder phase and reaction mechanism of fly ash systems are inherently different to that of metakaolin-based geopolymers. Although the inherent differences in the dissolution properties and phase composition of fly ash result in geopolymers that exhibit different properties, it is observed both in molecular structure and in microstructure that the same silicon and aluminum bonding and the same gel-phase binder are present in both systems.

2.3.2 Inactive Filler

Inactive filler is used for the purpose of supplying Al^{3+} ions to the geopolymerization process. It mainly consists of kaolinite or metakaolinite. The utilization of these inactive fillers is optional which is wholly dependent on the presence of Al^{3+} ions inside the synthesis process. In other words, raw materials which are enriched in Si^{4+} and Al^{3+} ions do not need the addition of inactive filler to complete the geopolymer process.

In the chemistry of geopolymer, Al^{3+} ions are needed to complete the sialate (silicon-oxo-aluminate) network. The sialate network consists of SiO^4 and AlO^4 tetrahedra linked alternately by sharing all oxygen atoms. Positive ions such as Na^+, K^+ and Ca^{2+}, must be present in the framework cavities to balance the negative charge of Al^{3+}. Mechanism of geopolymers involves the polycondensation reaction of geopolymeric precursor which is alumino-silicate oxide with alkali polysiliates yielding polymeric Si–O–Al bond as shown in Equation 2.1 (Davidovits, 1991, Van Jaarsveld et al., 1998).

$$M_n [- (Si - O_2)_z - Al - O]_n . wH_2O \quad \text{.....(2.1)}$$

Where M is the alkaline element, z is 1, 2 or 3 and n is the degree of polycondesation. The types of polysialates distinguished are illustrated in Figure 2.3 (Davidovits, 1988).

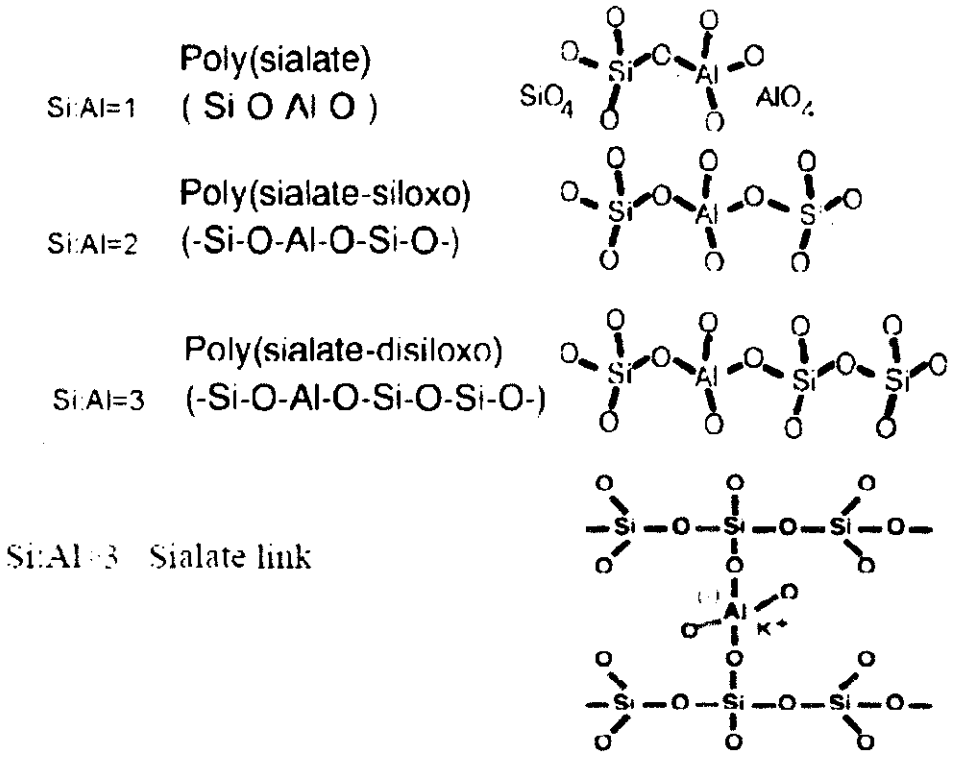

Figure 2.3: Types of Polysialates (Davidovits, 1988)

In this work, the source material which is fly ash will be studied to better understand about its composition. Based on the composition, the fly ash used contain sufficient percentage amount of aluminium oxide (AlO_4) which could be a good supplier of Al^{3+} ions for the geopolymer process. Hence, the addition of inactive filler is unnecessary in the synthesis.

2.3.3 Geopolymer Liquor

Geopolymer liquor is an alkali hydroxide solution required for the dissolution of raw materials while sodium or potassium silicate solution acts as a binder, alkali activator and dispersant or platiciser (Phair, 2001). The alkali component as an activator is a compound from the element of the first group in the periodic table, so such material is also called as alkali activated alumina-silicate binders or alkali activated cementitious material (Xiong CJ et al., 2004).

Strong alkalis are required to activate the silicon and aluminium present in the fly ash and setting additives, that allows transforming glassy structure partially or totally into a very compacted composite (Hardjito D et al., 2004). In theory, any alkali and alkali earth cation can be used as the alkali element in geopolymerization reactions. However, most of the studies have focused on the effect of potassium and sodium ions (Kostas et al., 2007). In addition, NaOH, Na_2SO_4, water-glass, Na_2CO_3, K_2CO_3, KOH, K_2SO_4 or a little amount of cement clinker (Xiong CJ et al., 2004). The choice of type of alkali metal cation used during geopolymer synthesis depends on many factors, the most important being the type of source materials as well as the foreseen application of the produced geopolymers (Van Jaarsveld, 2000). For instance, sodium silicate has been used for more than a century for the production of commercial products such as special cements, coatings, moulded articles and catalysts. Alkali metal cations control and affect almost all stages of geopolymerization and in particular during gel hardening and crystal formation making the cations an important contributor to the structure formation of geopolymers (Van Jaarsveld, 2000).

2.4 Synthesis Parameters

The properties of geopolymer are influenced by how the parameters during the synthesis process are being controlled. For instance, source materials with a high reactivity are required to produce a geopolymer with a high compressive strength (Alonso S, 2001). A study by Divya et al. (2007) presents the factors that affect unconfined compressive strength; curing temperature, curing time, silicate and hydroxide ratio, alkali concentration and pH. It can be concluded that the properties of the geopolymer is determined by the variations in the synthesis parameters.

Investigations into the underlying chemistry of the processes of setting and hardening development of geopolymer mixtures at the very early stage of geopolymerization, based on any kind of raw materials, is however rare in the literature. Such understanding is indeed important for geopolymer formation, which can be extremely sensitive to the type of raw materials used in its processing.

The setting time is mainly controlled by the alumina content and increases with increasing SiO_2/Al_2O_3 ratios in the initial mixture. However, if the Al_2O_3 content increases which lower the

SiO_2/Al_2O_3 ratios, the resulting products will acquire low strength (De Silva et al., 2007). Another study shows that the setting time of geopolymer decreased as the pH of activating solution increased. At lower pH values, the geopolymeric mix remained viscous and behaves like cement while at higher pH, the mix attained a more fluid gel composition, which was less viscous and more workable (Phair and Van Deventer, 2007).

Meanwhile, Zuhua Zhang et al. (2009) studied on the roles of water in the synthesis of calcined kaolin-based geopolymer. Since water plays an important role in the whole process of geopolymer synthesis, they had studied the geopolymer in term of the synthesis process itself. It is revealed that high liquid/solid ratio could accelerate the dissolution of raw materials and the hydrolysis of Si^{4+} and Al^{3+} compounds but hinder the polycondensation when OH^- concentration is as high as 12 M.

2.4.1 Silicate and Aluminium Ratio

In general, inorganic geopolymers can be synthesized by alkali activation of materials rich in SiO_2 and Al_2O_3. The mechanism involves the dissolution of Al and Si in the alkali medium, transportation (orientation) of dissolved species, followed by a polycondensation, forming a 3D network of silica-aluminate structures. The setting (hardening) of geopolymer is believed to be due to the polycondensation of hydrolysed aluminate and silicate species. Condensation can occur between aluminate and silicate species or silicate species themselves, depending on the concentration of Si in the system (De Silva et al., 2007).

De Silva et al. (2007) studied the effect of initial Si/Al ratio on the setting time based on metakaolin since the raw material is a good source of Al_2O_3 and SiO_2 which is highly reactive with alkaline activators. Typically, a mixture with SiO_2/Al_2O_3 ratios in the range of 3.4 - 3.8 with a Na_2O/Al_2O_3 ratio of about 1 provides better properties. Changes in the SiO_2/Al_2O_3 ratio beyond this range have been found to result in low strength systems. These initial ratios can be expected to change when materials other than metakaolin are used as the Al_2O_3 and SiO_2 sources.

2.4.2 pH Values

According to Phair and Van Deventer (2001), the most significant factor that controls the compressive strength of fly ash-based geopolymers is the pH of the initial alkali metal silicate precursor. When cement is used as a setting additive in the geopolymeric matrix the compressive strength increases almost exponentially with increasing pH. The higher alkali content was found to promote solid dissolution but also caused alumina-silicate gel precipitation at very early stages resulting thus in lower compressive strength (Lee and Van Deventer, 2002).

Strength at pH 14 was 50 times larger than those at pH 12 of geopolymeric matrix utilizing cement as setting additive. Higher solubility of monomers was expected by KOH than NaOH because of higher alkalinity. With increasing pH there was a predominance of smaller chain oligomers and monomeric silicate available to react with soluble aluminium. Further with increase in pH, soluble aluminium increases and reacts with calcium available for reaction (Phair and Van Deventer, 2001). Lower pH-value of the solution leads to lower monomer concentration. Figure 2.4 reveals the pH-value of the single alkaline solution, varying in concentration and kind of alkali ions. From the below observations it is clear that pH range 13–14 is most suitable for the formation of the geopolymers with better mechanical strength.

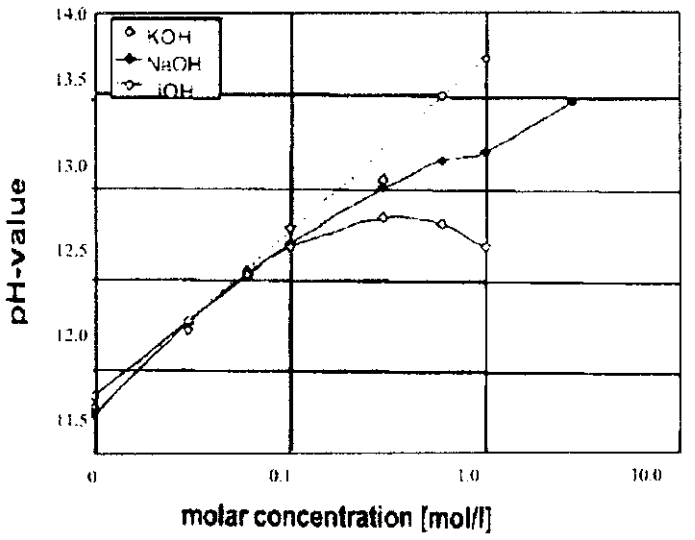

Figure 2.4: Influence of Concentration on pH value (Divya et al., 2007)

2.4.3 Roles of Water in Geopolymerization

Water plays an important role in the whole process of geopolymer synthesis. The geopolymerisation can be approximately partitioned into two periods: I dissolution–hydrolysis, II hydrolysis–polycondensation (Zuhua Zhang et al., 2009). When the solution concentration increases from 3 mol/L to 12 mol/L, NaOH solution of high concentration can activate the calcined kaolin quicker and stronger than the lower concentration, thus, quicker the setting time. Pure water cannot activate the solid material unless it contains considerable OH^- anion. In fact, high alkalinity is necessary to the activation of raw material (Van Deventer, 2003). In other words, too much water will reduce the geopolymerization for its dilution effect.

2.5 Applications of Geopolymer in Chronological Order

Geopolymer has been used in many applications since the early seventies. It has been proposed that the geopolymer has already been used since the ancient times of the Greeks and Egyptians (Davidovits, 1988). However, this report will only discuss the applications of geopolymer in modern times.

2.5.1 Geopolymer as Fire Resistant Wood Chipboards

In 1973 to 1976, the first applications were building products such as fire resistant chip board panels, comprised of a wooden core faced with two geopolymer composite coatings. An unusual feature was observed to characterize the manufacturing process: for the first time, the hardening of organic material (wood chips and organic resin) occurred simultaneously with the setting of the mineral silico-aluminate (Na-Poly(sialate)),when applying the same thermosetting parameters as for organic resin. Figure 2.5 shows fire resistant wood chipboard with geopolymer surfaces as facing.

Figure 2.5: Fire Resistant Wood Chipboard with Geopolymer facing

2.5.2 Geopolymer in Ceramic Applications

In 1977 to 1978, geopolymer was used in ceramic applications. Results were obtained with a natural kaolinite/quartz blend. In this natural blend, the quartz crystals are surrounded with kaolinite micelle. A nanocomposite called SILIFACE Q was obtained. It has exceptional temperature stability and very low thermal expansion. As a comparison, the mean linear thermal expansion between 20C to 700C for ferum is 0.96% while for SILIFACE is only 0.13%.This unique geopolymer was tested for manufacture of electrical fuses. The mechanical properties, thermal properties, molding at 120 C, post treatment at 450 C were excellent. Figure 2.6 below shows electrical fuses made of geopolymer.

Figure 2.6: Electrical fuses made of geopolymer SILIFACE

2.5.3 Geopolymer in Low Temperature Setting of Ceramic

In 1977 to 1982, geopolymer was used in Low Temperature Geopolymeric Setting (LTGS).It takes place at drying temperature (50 C to 250 C), in alkaline conditions, through an oligosialate precursor (-Si-O-Al-O-) in concentrations from 2 to 6 % by weight of the ceramic paste. The kaolinite in clays is transformed by LTGS into a three dimensional compound of the poly(sialate),stable to water and possessing high mechanical strength. LTGS may dramatically enhance and modernize the traditional ceramic industry. Once being geopolymerised into Na-polysialate or K-polysialate at 125 C to 250 C, the ceramic bodies may be rapidly fired at 1000 C to 1200 C to produce high quality ceramics. Figure 2.7 shows a brick made with Low Temperature Geopolymeric Setting.

Figure2.7: Brick made with LTGS

2.5.4 Geopolymer High Strength Cement

In 1983, geopolymer was used in production of high strength cement. It was discovered that the addition of ground blast furnace slag, which is a latent hydraulic cementitious product, to the poly(sialate) type of geopolymer, accelerates the setting time and significantly improves compressive and flexural strength. Geopolymer cements are acid-resistant cementitious materials. Geopolymerization involves the chemical reaction of aluminosilicate oxides with alkali and calcium polysilicates, yielding polymeric Si-O-Al bonds dissolved by acidic solutions.

Portland based cements (plain and slag blended) are destroyed in acidic environment. Calcium aluminate cement is expensive to produce, and does not behave satisfactorily, having 30 to 60% of weight loss (destruction). Figure 2.8 shows the application of geopolymer as pavement repair material.

Figure 2.8: Geopolymeric cement as pavement repair material

2.5.5 Geopolymer in Fireproof Fiber Reinforced Composites

In 1987 to 2000, geopolymers were used as fireproof fiber reinforced composites. In accidents when a plane crash-lands and catches fire, half the people who survive the impact may not get out in time. That is because the plastics in the cabin (the seat cushions, carpeting, walls and luggage bins) are combustible. And when they burn, they give off flammable gases that, in two minutes, can explode into a fireball. The U.S. Federal Aviation Administration (F.A.A.), wanted to give passengers more time to escape. The F.A.A. initiated a cooperative research program to develop low-cost, environmentally friendly, fire resistant matrix materials for aircraft composites and cabin interior applications. The GÉOPOLYMÈRE Composite has been selected by F.A.A. as the best candidate for this program. Figure 2.9 shows the composite being tested with fire.

Figure 2.9: Geopolymer composite resisting fire

2.6 Geopolymer as Steel Coating Materials

Steel is one of the most common engineering materials and thus its fire resistant properties are very vital. For instance, steel loses 50% of its room temperature yield stress at approximately 550°C (Jadambaa et al., 2011). Coating is defined as a covering that is applied to the surface of an object, usually referred to as the substrate. In many cases coatings are applied to improve surface properties of the substrate, such as appearance, adhesion, wettability, corrosion resistance, wear resistance, and scratch resistance.

In application of steel coatings, research development in geopolymer-based coatings is being conducted since it exhibits superior fire resistance properties as well as excellent adhesion to steel than existing coatings. In fact, geopolymers are also very promising material for protective coating of different surfaces including metal due to their superior mechanical, chemical and thermal resistance properties (Jadambaa et al., 2010).

2.6.1 Type of Coatings

Coatings are basically an applied layer to expand the durability and sturdiness of certain substrate. Thus, its anticorrosion, water resistance, fire resistance, adhesiveness and other related properties are important to perform as a good coating function. As for fire proof materials, the coatings are divided into different groups namely cementitious materials, intumescent paints, fibrous material etc. Of these materials, cementitious materials and intumescent paints are most commonly used.

a. Cementitious Materials

The cementitious materials are in general inorganic and as such do not combust when exposed to fire. Many studies have been done to improve its durability and wear resistance since these materials are low in cost. In its most basic form, the principle of cementitious materials is the normal mixing of producing Portland cement. Nowadays, the mixtures contain supplementary cementitious materials that make up a portion of cementitious component in mixing. These materials are generally by-product from other processes or natural materials.

Some of these materials are called pozzolans, which by themselves do not have any cementitious properties but when used with Portland cement, they react to form cementitious compounds. Other materials however, do exhibit cementitous properties (National Ready Mixed Concrete Association, 2007). Supplementary cementitious materials can be used to improve coating performance in its fresh and hardened state. They are primarily used to improved workability, durability and strength. Figure 2.10 shows some examples of cementitious materials.

Figure 2.10: Example of Cementitious Materials

However, as they are made from ordinary Portland Cement (OPC), they are likely to lose strength and adversely affected by spalling when exposed to fire; spall are flakes of a material that are broken off a larger solid body and can be produced by variety of mechanisms including as a result of projectile impact, corrosion weathering, cavitation etc. Spalling describes the process of surface failure in which spall is shed. Cementitious coatings also need to be thick, and thus heavy, if they are to provide adequate fire protection (Jadambaa et al., 2011).

b. Intumescent Paint

Thin film intumescent coatings are manufactured from organic materials and are inert at low temperatures. They swell (or intumesce) to provide a charred layer of low conductivity foam when exposed to high temperatures. This char layer reduces the rate of temperature rise in the steel and prolongs the steels load bearing capacity. It exhibits light, aesthetic and smooth properties, and can be used as thin coatings (Guojian and Jiayun, 2010).

Intumescent coatings can be applied off-site. This takes the application of fire protection off the critical path and helps to reduce the overall construction programme. A range of fully tested topcoats can be specified for use with intumescent coatings that offer a wide choice of finish in terms of colour and level of gloss. In addition, top coats can easily be repaired and redecorated. One of the most commonly used intumescent coating is a sodium silicate based paint.

The use of sodium silicate as a basis to produce a harder char which is suitable for the utilization for exterior steel fireproofing has been notified. In this application, it is necessary to produce a more substantial char, with a quantifiable expansion pressure. In the case of the exterior fireproofing, a hydrocarbon fire must be held off with quite potentially more kinetic energy than a house fire. Intumescent that produce hard chars are not typically used for interior spray fireproofing as they are not suitable for that application. Figure 2.11 shows pipes covered with intumescent paint.

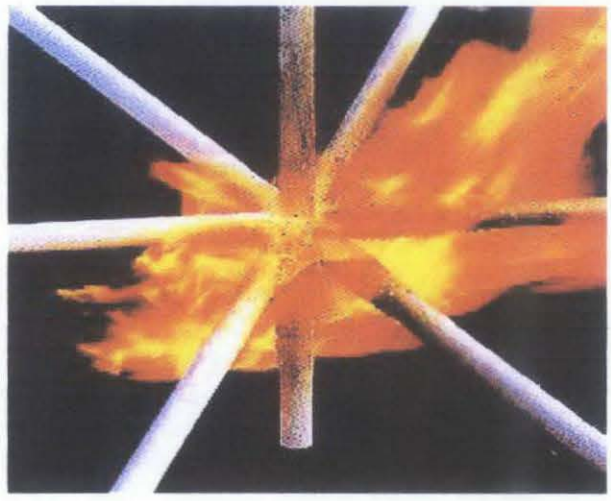

Figure 2.11: Pipes Covered With a Thin-Film Intumescent

However, the intumescent paint is more expensive and often requires extensive surface preparation before applying coating. Additionally, it has poor water resistance, low fire rating and may combine with carbon dioxide to revert back to its original constituents of silicon dioxide and sodium carbonate (Jadambaa, 2010).

2.6.2 Geopolymer-type Coating

Geopolymer is a man-made material with many exceptional properties including impressive fire resistance and capacity to encapsulate hazardous material (Davidovits, 2008). In the development of geopolymer coating, studies towards understanding this green novel technology is being extensively conducted. There are limited literatures on this subject matter with most of current studies been focused on the thermal and corrosion properties of the geopolymer-type coating.

Jadambaa et al. (2011) studied the fire resistivity properties of geopolymer-type coating by using the basis of metakaolin. The geopolymer-type coatings were prepared by using an industrially available silicate solution and metakaolin which was then applied to steel substrates. By taking H_2O and cement ratio as manipulated variable, they examined the coatings on the metal substrates on the basis of curing and hardening properties.

The studies showed that by using a geopolymer-type composition with a H_2O and cement of 0.41 shows improved water stability when compared with samples with a H_2O and cement of 0.5 which lost 34% of its weight after 72 hours static leaching in the water. Figure 2.12 presents the reduced weight changed for each coating samples. It can be concluded that even though the prepared coatings showed reduced water stability, their adhesion to metal substrates and thermal resistance were excellent.

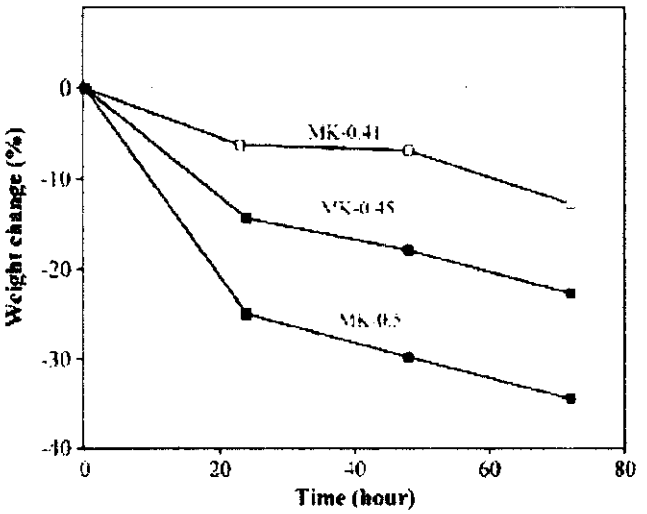

Figure 2.12: Weight Change vs. Time Curves of the Coated Samples (Jadambaa et al., 2011)

Another study on geopolymer-type coatings by Zhang et al. (2010) exposed the potential application of the materials for marine concrete. By using granulated blast furnace slag and metakaolin as raw materials, they studied the influence of microstructure to the anticorrosion property of geopolymers. The results revealed the mechanism accounting for the low water permeability, good anticorrosion in sea water and high bonding strength to paste and mortar. The physical anticorrosion was caused by the compact microstructure of geopolymer. The geopolymers were stable when immersed in sea water or exposed in air (unlike the hydration product of OPC), giving marine concrete a chemical protection.

A review on preparation of geopolymer-type coatings believed that water content of initial formulation plays a big role in the properties of resultant geopolymer. Based on synthesizing process of geopolymer from metakaolin, much water may be required due to porosity increase and therefore become too soft which is suitable for applications as adhesives, coatings and hydro-ceramics (Duxson et al., 2007). Van Jaarsveld et al (2002) also concluded that water content affected the properties of geopolymer. Further study by Van Jaarsveld et al (2003) showed that the source materials determine the properties of geopolymers, especially the water ratio. The above literatures suggested that the geopolymers can be used as coating materials based on its excellent properties. In this work however, the adhesive property of geopolymers will be tested against the different composition. As the coatings will be applied on steel

substrates, it is essential for the coating to have high adhesion strength for it to perform its fire resistant function. In fact, the fireproof effect of coating material is generally due to the formation of a heat insulating layer, a protective atmosphere and to the endothermic processes that lower the surface temperature (Jadambaa et al., 2009).

2.6 Studies on Corrosion

The corrosion of materials causes great loss in the industrial applications, especially under some extreme conditions, i.e. the corrosive atmosphere and high temperature. Corrosion can be defined as the deterioration of a material due to its reaction with its environment. Corrosion of iron or steel occurs due to the reaction of Fe with reactive species such as oxygen and water. Corrosion product or rust is formed and gradually appears on the surface of steel or low-alloyed steel when they are exposed to humid air at high temperature or even at room temperature. Generally, iron surface turns rusty in the presence of oxygen gas and water. A region of the metal's surface serves as an anode, where oxidation occurs. Then, the electrons given up by iron reduce atmospheric oxygen to water at the cathode which is another region of the same metal's surface. The reaction processes are shown in equations (2.2) and (2.3) below:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad (2.2)$$

$$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O + 4OH^{-} \quad (2.3)$$

The overall reaction is given by equation (2.4):

$$2Fe\,(s) + O_2\,(g) + 4H^{+}\,(aq) \rightarrow 2Fe^{2+}\,(aq) + 4H_2O\,(l) \quad (2.4)$$

This reaction is promoted in an acidic solution when H^{+} ions are supplied by the reaction of atmospheric carbon dioxide with water to form H_2CO_3. The Fe^{2+} ions formed at the anode will be further oxidized by oxygen. The oxidation of iron occurs as shown in equation (2.5):

$$2Fe^{2+}\,(aq) + O_2\,(g) + (4 + 2x)H_2O\,(l) \rightarrow 2Fe_2O_3 \,.\, xH_2O + 4H^{+}\,(aq) \quad (2.5)$$

The amount of water associated with iron (III) oxide or known as ferric oxide varies, so the formula of rust can be represented as $2Fe_2O_3.xH_2O$.The corrosion process may occur rapidly in acidic medium. Our environment is acidic due to dissolved gases such as carbon dioxide which may produce carbonic acid when reacted with water. To prevent corrosion, we can choose to condition the metal, to condition the environment or to control it electrochemically. Conditioning the environment may be achieved through the medium of removal of oxygen and usage of corrosion inhibitors. Electrochemical corrosion control can be achieved by anodic and cathodic protection. We may choose to condition the metal; to alloy the metal or to coat the metal. In this project, we choose the latter approach which is coating the metal.

In the instance of corrosion, the protection may aim to prohibit contact of the coating with oxygen or water – each a necessary element of the corrosion reaction. The aim may also be to prohibit contact with corrosion catalysts which are salts, acids or alkalis. Examples of the barrier coatings are fairly straightforward. Impervious coating like the wax, polyethylene, coal tar and asphalt is aimed at prevention of water permeation to the metal surface as water is a specific corrosive substance. Other coatings aim to prohibit oxygen permeation. In both cases, the coatings are diffusion barriers and the key is to have a coating that dissolves as little as possible of permeate within the coating and also inhibits permeation. For this project, we plan to use fly ash based geopolymer as the coating material.

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CHAPTER 3

METHODOLOGY

3.1 Project Activities

The research methodology for this project is divided into two phases where phase one mainly involves literature review. The second phase is the most important part of the entire project which the actual work on developing the geopolymer formulation is executed. This project will mainly focus on synthesizing the geopolymer by using fly ash as the raw material. This research project will be conducted in several stages which begin with raw material preparation and characterization, geopolymer synthesis and ends with determination of the properties of geopolymer produced. Figure 3.1 presents the simplified version of project activities for this work and Figure 3.2 shows the Gantt Chart for this project.

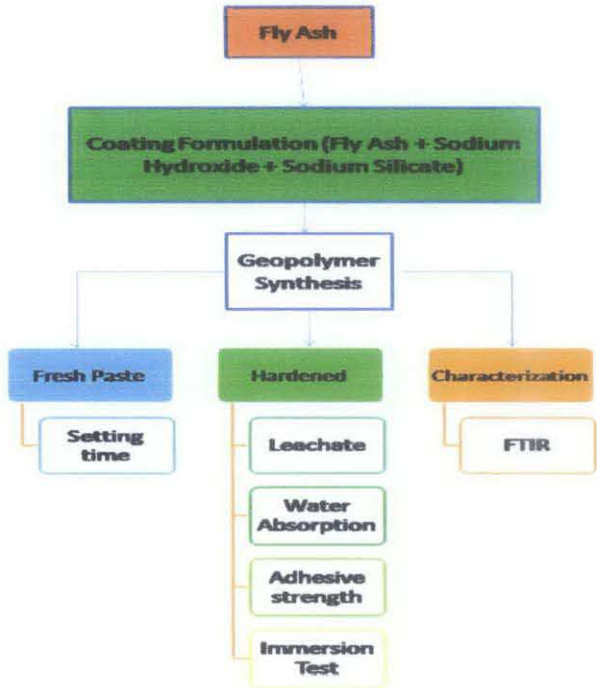

Figure 3.1: Flowchart of Project Activities

No	Detail/Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Project Work Continues															
2	Progress Report Submission															
3	Project Work Continues															
4	Pre-EDX															
5	Draft Report Submission															
6	Dissertation Submission (soft copy)								**Break**							
7	Submission of Technical Paper															
8	Oral Presentation															
9	Project Dissertation Submission (hardbound)															

Figure 3.2 Gantt Chart for FYP II

Process **Key Milestones**

3.2 Raw Material Preparation and Characterization

The first activity will involve with preparation and characterization of the raw material. The raw material which is fly ash is obtained from China and representatively sampled for characterization work. The sample is dried under the temperature of 120°C for 24 hours before further work is done. The characterization work will be done by using Fourier Transform Infrared (FTIR) Spectroscopy.

3.3 Experimental Procedures

The experiments were executed according to the following procedures. The fly ash used is supplied by Tangshan Tongshun Industry from Hebei Province of China. Below is Table 3.1 which shows the chemical composition of the fly ash used in the experiments:

Table 3.1: The Chemical Composition of the Fly Ash

Component	Weight percent (%)
SiO_2 - Amorphous	35.0 – 60.0
SiO_2 - Crystalline	3.00 – 7.00
Fe_2O_3	3.00 – 20.0
CaO	1.00 – 10.0
MgO	0.50 – 5.00
Al_2O_3	15.0 – 30.0
K_2O	0.10 – 1.00
Na_2O	0.50 – 5.00
TiO_2	0.50 – 5.00

To optimize fly ash based geopolymer for corrosion resistant coating, some essential data are needed. This project will provide necessary information regarding characterization, setting time, density change, chemical leaching, compressive strength, adhesive strength and water absorption. The volume of data in the field of aluminosilicate dissolution and weathering represents a whole field of scientific endeavor in itself, and is not part of the scope of this project. The solid part of the mixture is fly ash and the liquid part of the mixture is NaOH solution and Na_2SiO_3 solution. The biomass model as modification of the geopolymer consists of starch and lignin with equal proportion of each other. The sodium hydroxide (NaOH) solids were dissolved in water to make the solution. The mass of NaOH solids in a solution varied depending on the concentration of the solution expressed in terms of molar, M. For instance, NaOH solution with a concentration of 12 M consisted of 12 x 40 = 480 grams of NaOH solids (in flake or pellet

form) per litre of the solution, where 40 is the molecular weight of NaOH. In preparation of NaOH solution, 480 g of NaOH pellets of 99% purity was dissolved in one liter of distilled water in a volumetric flask to get 12 M concentration of NaOH. Alkaline activator which is combination of NaOH and Na_2SiO_3 was prepared just before mixing with fly ash. The addition of sodium silicate is to enhance the process of geopolymerization process (Xu and Deventer, 2000). The ratio of fly ash/alkaline activator and Na_2SiO_3/NaOH is 2.5 and fixed for all mixture. The use of this ratio is due to Hardjito et al. (2008) which stated that ratio of fly ash/alkaline activator of 2.5 produced the highest compressive strength at 28th day of testing. Hardjito et al. (2004) used ratio of Na_2SiO_3/NaOH 2.5 and 0.4 in the preparation for geopolymer concrete. The geopolymer is prepared by first weighing the corresponding amount of fly ash needed. The weighed fly ash and alkaline activator were mixed together in the mixer at low mixing speed for about 5 minutes until homogeneous paste was obtained.

Casting and curing

The geopolymer paste was placed in 50 x 50 x 50mm cube mould and cured in the oven for 2 days at constant temperature of 70°C. These geopolymer cubes are the representative samples to test compressive strength, water absorption and leachate of the geopolymer.

Steel plates (A-36 type with 98% Fe) with approximate dimensions of 3 x 4 cm were cleaned with abrasive paper and polishing machine followed by washing with detergent, sodium hydroxide, mild acid and de-ionised water. Geopolymer compositions were applied to metal substrates and followed by curing at 70°C for 2 days.

Setting time

This experiment is to study on the effect of setting time due to biomass addition in the formation of fly ash-based geopolymer at different weight percentage ranging from 1% to 4%. Since the geopolymer will be used in application of coating, the setting time should be prolonged to a range within a half of hour. Too short of setting time will result in less suitability to be used in real site. In order to observe the changes in the setting time, another process parameter is made constant which is solid to liquid ratio. The study for this particular parameter is began with the used of 100% fly ash as the raw material which is also functioned as the control mix for the whole experiment. Then, a series of fresh paste with different percentage of biomass is prepared.

Total time taken for mixture reaching its harden state is measured as setting time. The setting time of the control mix and the setting time of the mixtures with addition of biomass model will be compared.

Compressive Strength Test

The procedures to prepare the geopolymer mixture have been explained above. After mixing the geopolymer, they will be cured at different temperatures to test the compressive strength of the geopolymers. One batch is cured at elevated temperature and another batch is cured at ambient temperature. The resultant geopolymers are left for 7 days before being tested for its compressive strength. The geopolymers were taken out from the moulds and were tested using Universal Testing Machine. The compressive strength of the geopolymers with different curing temperatures will be compared.

Leachate Test

The methods to prepare the geopolymer mixture have been explained earlier. The casted and cured geopolymers were soaked in water for 30 days. After 30 days, the water will be analyzed to know the concentration of leachate produced by the geopolymer mixture.

Immersion Test

Firstly, the steel plates (A-36 type with 98% Fe) with approximate dimensions of 3 x 4 cm will be cleaned by abrasive paper, followed by detergent, sodium hydroxide, mild acid and de-ionised water washing. Geopolymer pastes prepared from the respective fly ash mixture will then be applied to steel substrates by dipping the metal into the geopolymer mix. This will be followed by curing at elevated temperature of 70°C.The coated metal substrates then will be immersed in corrosion catalysts solutions of Na_2SO_4, $MgSO_4$, and NaCl. The planned period of immersion is two months and the corrosion catalysts solutions will be replenished after 30 days.

Adhesive Strength Test

The methods to prepare the geopolymer mixture and to coat the steel plates have been explained above. The coated steel plates will be tested with Elcometer 106 to determine the adhesive strength. The surface under examination is prepared and then a test dolly is attached by adhesive. When the adhesive is cured after 24 hours, the Adhesion Tester claw is engaged onto the dolly and a force is applied by tightening a wheel on top of the tester. The adhesive strength is the amount of force applied to pull off the coating from the metal substrates.

3.4 Materials and Equipments

Below is Table 3.2 which shows materials and equipments required for the experiments.

Table 3.2: Materials and Equipments

Chemicals	**Equipments/Materials**
Fly Ash (Class F)	FTIR – Fourier Transform Infra Red
Sodium Sulfate - Na_2SO_4	Metal slabs (steel)
Magnesium Sulfate - $MgSO_4$	Mixer
Sodium Chloride - NaCl	Paint brushes
Sodium Hydroxide - NaOH	Electric heater & stirrer
Sodium Silicate - Na_2SiO_3	Digital thermometer
	Conical flask, beakers
	Elcometer
	Safety mask, goggle, dust mask

The salt solutions that act as corrosion catalysts and their respective concentrations are Na_2SO_4, $MgSO_4$, NaCl and 44, 5,164g/dm^3. The salt solutions used are in accordance with CSN-EN 206-1 European Standard. The solutions are replenished after 30 days to maintain concentrations.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Fourier Transform Infra Red Spectroscopy

Geopolymeric compounds are either crystalline or non-crystalline (amorphous or glassy structure).Their structure can be investigated from Fourier Transform infrared spectroscopy. The result of the spectroscopy deal with the behavior of the main (Si,Al-O) band, which is found at about 1000 cm-1.An approximate relationship between the frequency of this band and the ratio of Si:Al in the aluminosilicate framework was observed by Milkey (1960), the higher the Al inclusions, the lower the wave length. Interpretations of these spectra were based on assignment of the infrared bands to certain structural groups in the various zeolite frameworks. In order to conduct this assignment on geopolymers, it is necessary to know the basic polymeric structure. The spectra are determined for the samples on Perkin Elmer spectrometer using the KBr pellet technique. The IR spectra for poly(sialate), poly(sialate-siloxo) as well as for geopolymeric precursors consist of the strongest vibrations found in all aluminosilicates, which are assigned to internal vibrations of Si-O-Si, Si-O-Al and are found at 950 – 1250 cm^{-1} and at 420-500 cm^{-1}.The stretching modes are sensitive to the Si:Al composition of the framework and may shift to a lower frequency with increasing number of tetrahedral aluminium atoms. The table below shows IR characteristic bands and corresponding species of geopolymeric precursor and geopolymers, after Barbosa et al.(2000).

Table 4.1: IR Characteristic Bands and Corresponding Species

Si-O	1080 – 1100 cm^{-1}	Symmetrical vibration
Si(Al)-O	1008 cm^{-1}	Asymmetrical vibration
Al-OH	914 cm^{-1}	6 coordinated Al-OH stretching vibration
Si-OH	840 cm^{-1}	Bending vibration
Al-O	798 cm^{-1}	4 coordinated Al-O stretching vibration
Si-O	694 cm^{-1}	Symmetrically stretching vibration
Si-O-Al	540 cm^{-1}	Bending vibration
Si-O	469 cm^{-1}	In-plane bending vibration

The strong band at 1500-2800 cm^{-1} in the IR spectrum of fly ash remains. The geopolymerization of fly ash shifts it towards low wave number. The shift is approximately 90-100 cm^{-1}.This demonstrates that an obvious change in the microstructure takes place during geopolymerization reaction, resulting in a formation of new products with different microstructure from fly ash material. The large shift toward the low wave number may be attributed to the partial replacement of SiO_4 species by AlO_4, resulting in a change in the local chemical environment of Si-O bond.

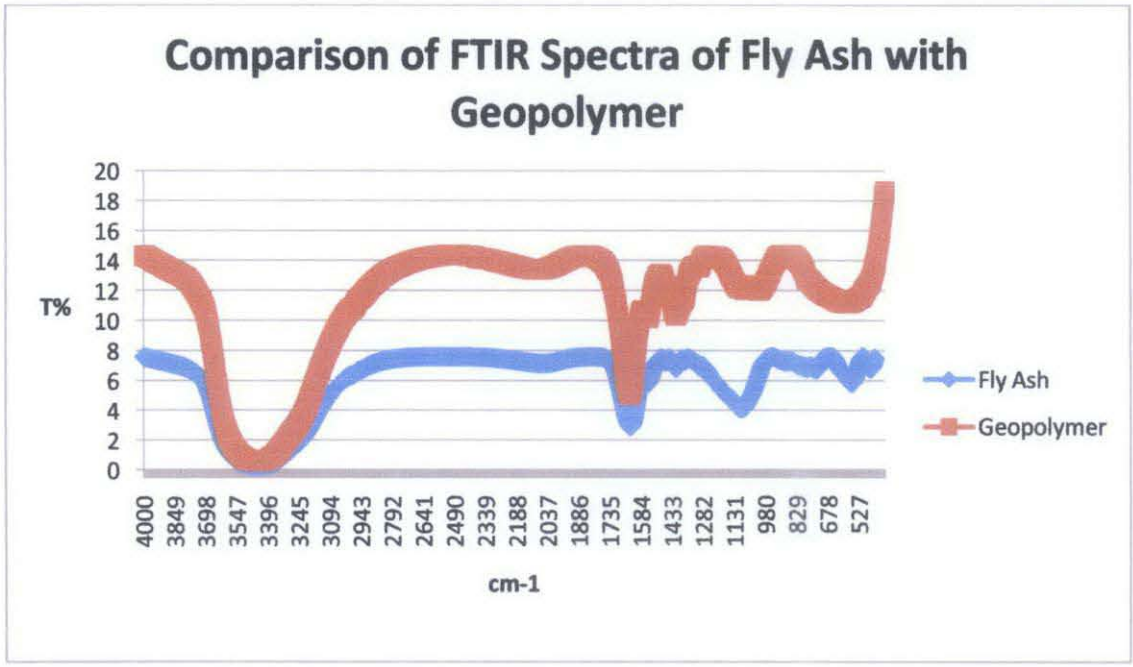

Figure 4.1: Comparison of FTIR Spectrum of Fly Ash with Geopolymer

4.2 Compressive Strength

The compressive strength test was performed on a 2000 kN capacity Compression Machine (MS Instrument Sdn Bhd) Model ELE ADR 2000. Figure 4.2 below shows the 2000 kN Compression Machine used.

Figure 4.2: ELE ADR 2000 used in compressive strength test

The compressive strength of the geopolymer is measured when the samples break under the compressive force. Figure 4.3 shows broken samples after being compressed by 2000 kN force.

Figure 4.3: Geopolymer Samples after Compressive Strength Test

A comparison between elevated temperature cured geopolymer and ambient temperature cured geopolymer has indicated that elevated temperature curing produces geopolymer with greater compressive strength. The early strength was measured after 7 days and the second measurement was done after the geopolymer aged for 100 days. The following tables (Table 4.2 and 4.3) and figures (Figure 4.4 and 4.5) show the results of the compressive strength.

Table 4.2: Geopolymer Compressive Strength for Ambient Temperature Curing

	Compressive Strength (Mpa)	Compressive Strength after 100 days (Mpa)	Percentage Increase (%)
Ambient Sample 1	13.27	13.83	4.220045215
Ambient Sample 2	11.05	13.56	22.71493213
Ambient Sample 3	11.24	13.40	19.21708185

Table 4.3: Geopolymer Compressive Strength for Elevated Temperature Curing

	Compressive Strength (Mpa)	Compressive Strength after 100 days (Mpa)	Percentage Increase (%)
Oven Sample 1	42.01	61.88	47.29826232
Oven Sample 2	55.46	70.27	26.70393076
Oven Sample 3	56.00	76.25	36.16071429

From the result, we know that curing at elevated temperature (70 C) is better than curing at ambient temperature to produce stronger geopolymers.

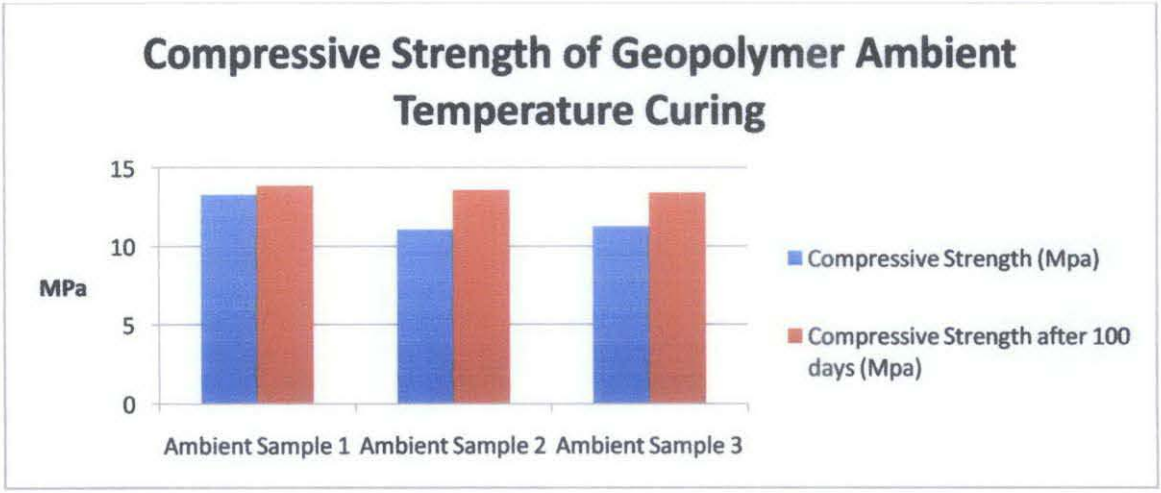

Figure 4.4: Geopolymer Compressive Strength Comparison (Ambient Temperature Curing)

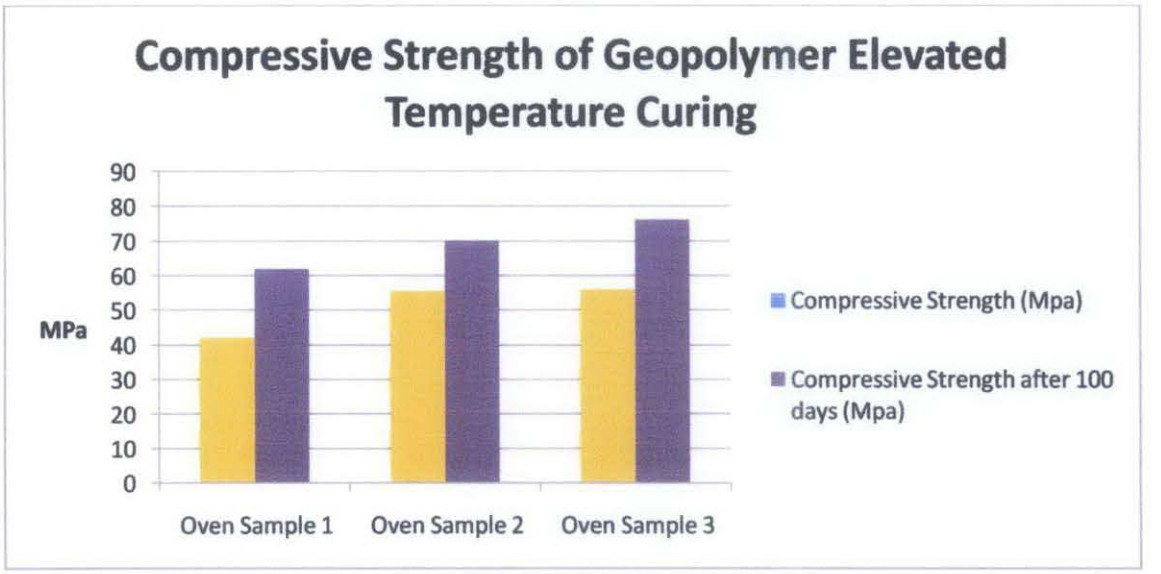

Figure 4.5: Geopolymer Compressive Strength Comparison (Elevated Temperature Curing)

4.3 Density

A study on geopolymer-type coatings by Zhang et al. (2010) exposed the potential application of the materials for marine concrete. The physical anticorrosion was caused by the compact microstructure of geopolymer. For corrosion resistant coatings, it is desirable to have high density. Higher density can give physical anticorrosion property to the geopolymer. It is important to have high density geopolymer as we can't add aggregates in the mixture. Density of the geopolymer material has been calculated and shown in Table 4.4. The highest density recorded is 1616kg/m^3.

Table 4.4: Density of the Geopolymer

Group	Designation of sample	Density before test (kg/m^3)	Density after test (kg/m^3)
1	A	1440	1600
	B	1464	1616
	C	1472	1616
2	D	1400	1544
	E	1448	1584
	F	1432	1584
3	G	1408	1568
	H	1432	1584
	I	1432	1584
4	J	1424	1552
	K	1392	1528
	L	1432	1576

Figure 4.6 below shows the density change of geopolymer before and after the water absorption test.

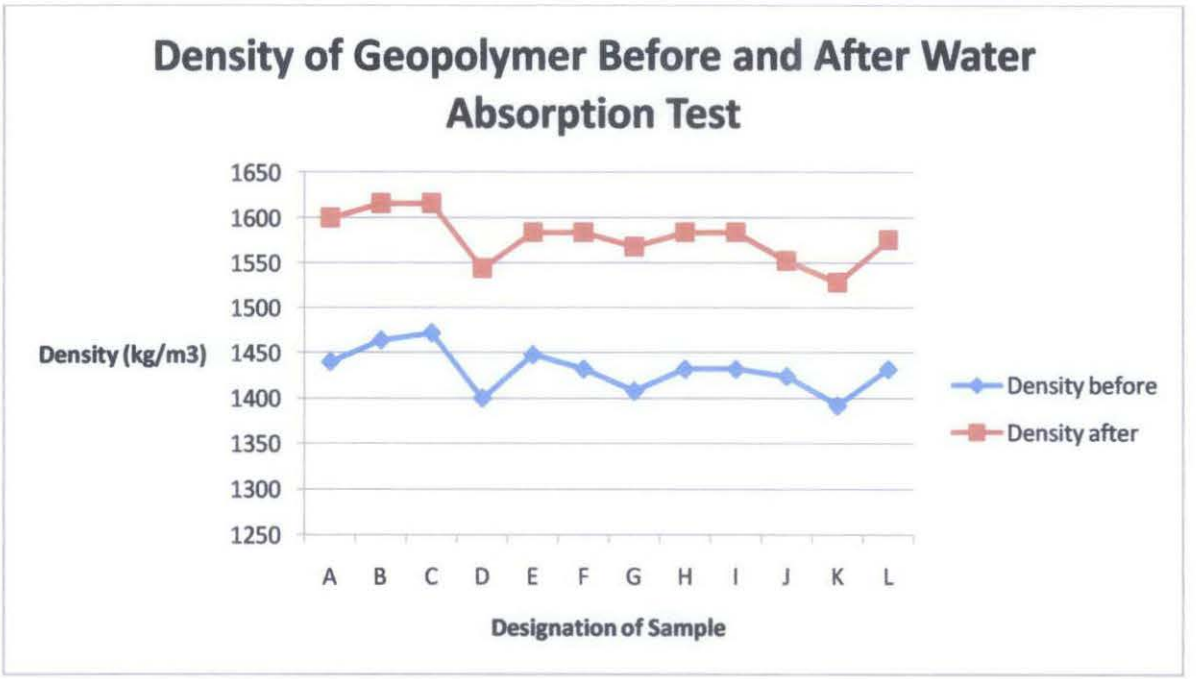

Figure 4.6: Density of Geopolymer Before and After

4.4 Water Absorption and Leachate Test

The water was titrated against 50 ml HCl at 1 M concentration and the concentration of leachate in the water after 30 days is less than 1 M. This concentration is small hence the geopolymer has low chemical leaching and this is a desirable property due to environmental concerns.

Dissolution of geopolymer in water is indicative of non-fully condensed and the likelihood of the presence of sodium silicate. By measuring the weight change, we can know the dissolution of the geopolymer. Dissolution of the geopolymer structure can cause crack formation and expose the metal surface to corrosive environment. Steel coated with fly ash based geopolymer should show high structural integrity with no evidence of crack formation. Maintaining structural integrity is an important and essential requirement of geopolymer coating.

Table 4.5 shows the weight change of the geopolymer after 30 days.

Table 4.5: Weight Change of the Geopolymer

Batch	Weight before absorption test (kg)	Weight after absorption test (kg)	Water absorbed (kg)
1	0.180	0.200	0.020
	0.183	0.202	0.019
	0.184	0.202	0.018
2	0.175	0.193	0.018
	0.181	0.198	0.017
	0.179	0.198	0.019
3	0.176	0.196	0.020
	0.179	0.198	0.019
	0.179	0.198	0.019
4	0.178	0.194	0.016
	0.174	0.191	0.017
	0.179	0.197	0.018

Figure 4.7 shows the weight change of geopolymer before and after the water absorption test.

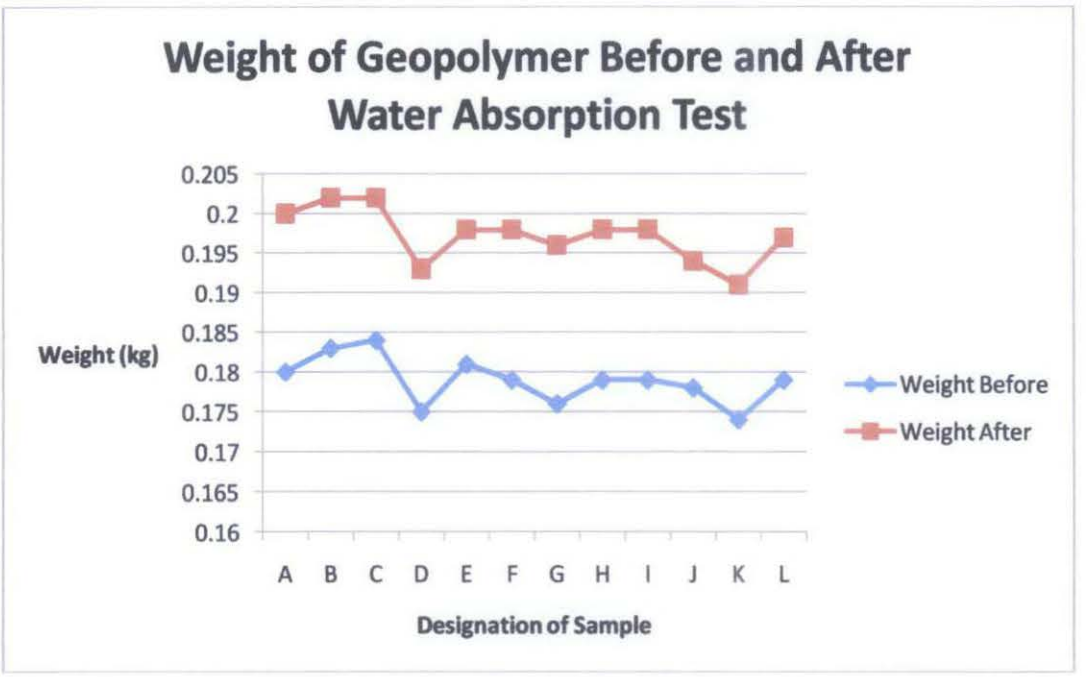

Figure 4.7: Weight of Geopolymer Before and After

Water is released during the chemical reaction that occurs in the formation of geopolymers. This water, expelled from the geopoylmer matrix during the curing and further drying periods, leaves behind discontinuous nano pores in the matrix, which provide benefits to the performance of geopolymers. The water in a geopolymer mixture, therefore, plays no role in the chemical reaction that takes place; it merely provides the workability to the mixture during handling. These nano pores is filled with water when the geopolymers were immersed in water. Based on the water stability behavior, it is thought that the dissolution of the aluminium cations into sodium silicate is the key factor for the formation of the condensed structure and high water stability implied a stronger condensed structure. A stronger condensed structure provides anticorrosion property to the geopolymer coating.

4.5 Setting Time

The setting time for each mixture is then determined by using Vicat apparatus. The time is taken until the geopolymer begin to harden; where the penetration is less than 10mm. The setting time for blank sample (100% fly ash) is 60 minutes. It is observed that the setting time has decreased by adding the biomass into the mixture. The influence of the biomass to decrease the setting time is subject to further and more thorough investigation. The setting time of the geopolymer is shown in Table 4.6 and Figure 4.8 below.

Table 4.6: Setting time of the Geopolymer

Composition	Setting time (minutes)
Lignin (1%), Starch (1%)	55
Lignin (2%), Starch (2%)	46
Lignin (3%), Starch (3%)	44
Lignin (4%), Starch (4%)	35

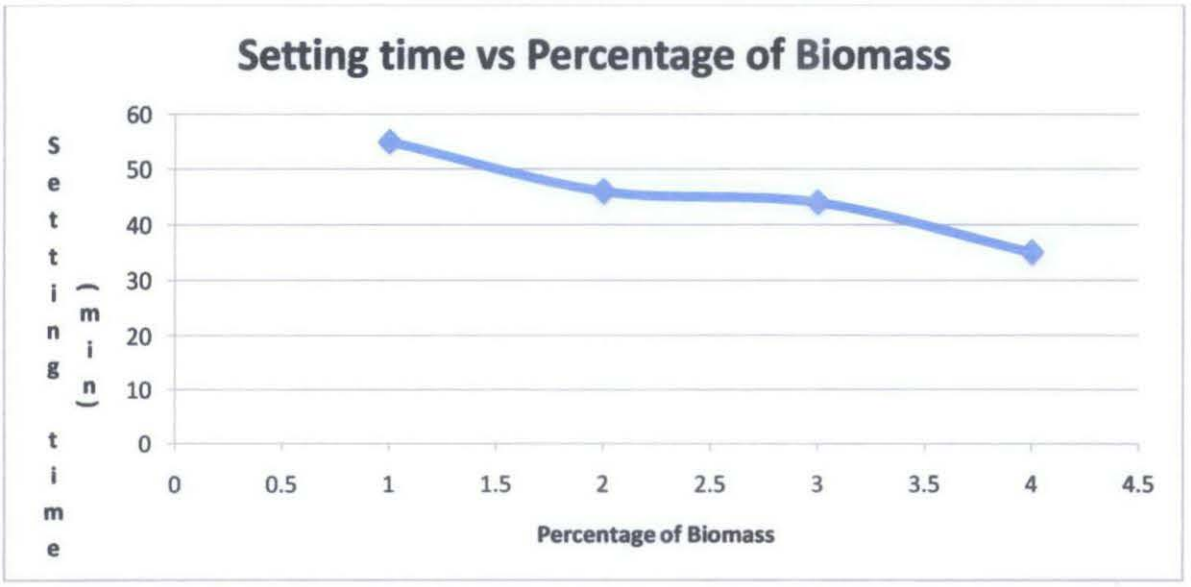

Figure 4.8: Setting time of the Geopolymer

4.6 Adhesive Strength

The equipment used to test the adhesive strength is Elcometer 106 Pull Off Adhesion Tester. It employs a pull-off method to measure the force required to pull an area of coating away from the base material. The force is recorded by means of a dragging indicator on an engraved scale. The indicator retains the value at which the dolly and the coating separate from the surface. The coating had fully adhered to the dolly and the test can be claimed as valid. From the literature, there is no clear consensus on the mechanism responsible for adhesion of geopolymeric gel to steel. Yong et al. suggested that the growth of synthetic geopolymeric gel is more rapid when placed on iron substrates due to chemical bonding. Latella et al. suggested that for metakaolin based geopolymer on stainless steel the bonding appears to be purely mechanical rather than chemical.

It is speculated that adhesion of the geopolymer compositions to stainless steel is likely to be physical; while the bonding to mild steel may have a component of chemical adhesion. However, we do not have direct evidence of the chemical bonding between geopolymer composition and mild steel substrates. The detailed mechanisms of the fly ash based geopolymer bonding to steel substrates are subject to further investigation. Table 4.7 shows the adhesive strength of the coatings with variable composition of biomass model.

Table 4.7: Adhesive Strength of the Coatings

Composition	Adhesive Strength (MPa)
Lignin (1%), Starch (1%)	0.1
Lignin (2%), Starch (2%)	0.1
Lignin (3%), Starch (3%)	0.1
Lignin (4%), Starch (4%)	0.1

4.7 Immersion Test

Twelve steel plates (A-36 type with 98% Fe) with approximate dimensions of 3 x 4 cm had been cleaned by abrasive paper, followed by detergent, sodium hydroxide, mild acid and de-ionised water washing. Geopolymer pastes prepared from the respective fly ash mixture were applied to steel substrates by dipping the metal into the geopolymer mix. This was followed by curing at elevated temperature of 70°C.The coated metal substrates then were immersed in corrosion catalysts solutions of Na_2SO_4, $MgSO_4$, NaCl and their respective concentrations are 44, 5, and 164g/dm^3. The planned period of immersion is two months and the corrosion catalysts solutions are replenished after 30 days to maintain their concentrations.

Figure 4.9: Steel plate coated with Fly Ash based Geopolymer

The result is that the specimens had no change of their appearance and had a small increase in mass. The visual appearance of the coatings after the immersion test reveals that there was no change in the appearance of the coatings compared to the condition before they were exposed. There are no sign of surface erosion, cracking or spalling on the coatings. The coating samples had some softening of the surface layer when exposed to the solutions but the damage does not ruin the whole geopolymer structure. It is expected that the action of the solutions on the geopolymer coating consists in an attack on the components of the geopolymer. The unreacted calcium in the geopolymer matrix will be converted to calcium salts of the solutions. As a result

of the conversion, the binding capacity of the hardened geopolymer is destroyed. The calcium salts are soluble and leaves the geopolymer body causing the coating to lose structural integrity. As a result, the coating surface becomes soft and could be removed, thus exposing the metal surface to corrosion. The fly ash used is Class F and has less than 10% CaO. Hence, the structure of the geopolymer did not get attacked by the solutions. This is the reason why Class F with less than 10% CaO is superior to Class C fly ash as base material for corrosion resistant coating.

Various studies have been reported to identify the role of fly ash as supplementary cementing material in Portland cement concrete in improving the sulfate resistance concrete. Some important factors identified which contributes to better resistance to sulfate attack include the low content of calcium oxide in fly ash or calcium hydroxide in concrete and the fine and discontinuous pore structure that results in low permeability. Fly ash based geopolymer undergoes a different mechanism to that of Portland cement concrete. The main product of geopolymerisation is not susceptible to sulfate attack. Sulfate attack can form expansive gypsum and ettringite (calcium sulfoaluminate) which can cause expansion, cracking and spalling in the concrete. The gypsum and ettringite could absorb moisture so that their volume of solid phase could increase to about 124% and 227%. The sulfate attack could lower the stiffness of the cement paste and increase the water absorption capacity of the paste. In other words, the coating could spall from the substrate. Besides the disruptive expansion and cracking, sulfate attack could also cause loss of cohesion between the coating and the substrates. Because there is generally no gypsum or ettringite formation in the main products of geopolymerisation, there is no mechanism of sulfate attack in fly ash based geopolymer. However, to some extent, the formation of gypsum and ettringite might happen depending on the presence of calcium in the geopolymer. The source of calcium could be from the unreacted fly ash. The extent of geopolymerization can be maximized by correct mix and processing design.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

This project focuses on conducting experiments to test a hypothesis; whether fly-ash based geopolymer is a feasible material for corrosion resistant coating or not. The developed geopolymer has high compressive strength, little chemical leaching, low water absorption, short setting time and increasing density pattern. Based on the results, it is believed that fly ash based geopolymer is feasible to be used as the material for corrosion resistant coating. The formulation can be further optimized and refined. There are several recommendations and suggestions for this project. The forced mixer type should be used in mixing the geopolymer materials, instead of the gravity type mixer. This would reduce the mixing time as an increase in mixing time increases the temperature of the fresh paste and hence reduce the workability. To improve the workability, it is suggested the use of admixtures to reduce the viscosity and cohesion. Several suggestions can be offered for future work and for expansion and continuation of this project. Firstly, the experiments can be implemented using few other types of corrosion catalysts like sulfonic acid. This should be done to see the effect of organic acid on the fly ash based geopolymer coating. Secondly, research should be concentrated on the improvement of the geopolymer mixing process, suitable admixtures formulation, coating process efficiency and the effect of corrosion product towards environment. Thirdly, the adhesive strength of the geopolymer coating needs to be improved. This can be done by researching the effect of solid to liquid ratio on the adhesive strength. Fourthly, the mechanisms of the setting process of the geopolymer with the addition of the biomass needs to be researched further. Fifthly, a material that can fill the nano pores left behind in the geopolymer body due to water loss during curing process needs to be researched. Lastly, besides the coating itself, other factors should also be considered as they may affect the corrosion rate of the steel substrates. Thus, it is crucial to investigate the effect of temperature, particle size, and other factors. The objectives of this project have been met.

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APPENDICES

Fresh Geopolymer Mix

Fresh Geopolymer Paste

Specimens Soaked in Water for Water Absorption Test

Class F Fly Ash Used in the Geopolymer Development

Geopolymer Paste in Moulds before Curing in the Oven

Geopolymer Hardened Cubes